ELECTRONIC STATE AND SUPERCONDUCTIVITY OF $YBa_2Cu_{3-x}M_xO_{7-y}$ (M=Al, Zn and Sn) SYSTEMS

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A series of $YBa_2Cu_{3-x}M_xO_{7-y}$ (M=Al, Zn and Sn) single-phase samples are prepared, and the measurements of the crystal structure, oxygen content, electric resistivity, thermoelectric power, Mössbauer spectrum, XPS and superconductivity have been performed. The experimental results of X-ray powder diffraction, Mössbauer spectrum and oxygen content show that the Zn^{2+} and the Al^{3+} occupy the Cu(2) site in Cu-O planes and the Cu(1) site in Cu-O chains respectively, but the Sn^{4+} occupies both the Cu(1) and Cu(2) sites. As regards the properties in superconducting state, both the Zn^{2+} and the Al^{3+} depress T_c strongly, but the Sn^{4+} does not. As for the electronic transport properties in normal state, the system doped by Al^{3+} displays a rapid increase of resistivity and some electron-localization-like effects, and the thermoelectric power enhances obviously; the series contained Zn^{2+} almost shows no changes of electric resistivity but the sign of the thermoelectric power is reversed. The experimental results also reveal that, although both the replacements for Cu(1) and for Cu(2) can suppress T_c and modify the electronic structure, the mechanism in these two kinds of replacements is not the same. The substitution of Al^{3+} for Cu(1) waekens the coupling intensity between the Cu-O planes, making the electron energy band narrow and the electrons localized; the replacement for Cu(2) with Zn^{2+} mainly influences the Cu-O plane itself, changing the structure of the Fermi surface. The simultaneous substitution of Sn^{4+} for Cu(1) and Cu(2) make the electronic structure vary complexly: sometimes it makes T_c high, sometimes low, depending on the preparation conditions. In additions, another noticeable phenomenon in this substitution study is the appearance of the Cu^{3+} oxidation state. Our XPS study shows when the Cu(1) was replaced by Al^{3+} or by Sn^{4+}, a peak corresponding to the Cu^{3+} oxidation state appears in the core level spectrum Cu_{2p}, but this phenomenon can not be observed in Zn-doped system. As we all know, it was believed that the presence of the Cu^{3+} plays a predominat role on high-T_c superconductivity, and the most probable candidate of the Cu^{3+} is at the Cu(1) site. The XPS data show that the Cu^{3+} do exist in the Cu(1) site. Unfortunately, our experimental results also reveal that there is no intrinsic relationship between the Cu^{3+} oxidation state and the high-T_c superconductivity. Observing and studying all our results noted above, at least one conclusion can be drawn as the following: intact Cu-O planes and strong coupling between these planes are two absolutely necessary conditions for the high-T_c superconductivity in 1:2:3 compounds.